Supplementary information

S1: Estimation of the dissolved organic mass (DOM) concentrations in aqueous solutions after SOA extraction

The DOM concentrations in aqueous solutions were calculated as follows:

$$DOM (mg/L) = \frac{1}{V_{water}} \times \frac{V_{sample}}{t_{sample}} \times \sum \left( \frac{m_i}{V_t} \right) \times \Delta t_i \times 80\%$$

Where:
- $V_{water}$ = volume of water used for SOA extraction (160 mL of water)
- $V_{sample}$ = volume of {air + particles} sampled from the chamber (0.720 m$^3$ of air)
- $t_{sample}$ = Sampling duration (2 hours)
- $\frac{V_{sample}}{t_{sample}} \times \sum \left( \frac{m_i}{V_t} \right) \times \Delta t_i$ = total mass of particles sampled on the filter (µg). The HR-AMS provided a mass of organic particles per m$^3$ every 2 minutes ($\frac{m_i}{V_t}$). Integrating this data during the filter collection time, multiplied by $\frac{V_{sample}}{t_{sample}}$, yields the total mass of particles sampled on the filter.
- The collection efficiency of SOA in water extracts was approximately 80%, as determined during previous experiments for SOA derived from α-pinene and isoprene.
Figure S1: Evolution of the number size distribution (analyzed by SMPS) of the SOA formed in the smog chamber as a function of the reaction time during the gas-phase photooxidation of (a): isoprene experiment 1 and (b): experiment 2. The dashed lines indicate the filter sampling start and end times.
Figure S2: TD-API-AMS measurements (a) in the negative mode and (b) in the positive mode of the chemical composition of SOA formed during isoprene photooxidation (experiment 1). Correlation between on-line (direct on-line measurement in the smog chamber) and off-line analysis (nebulization of “control” samples).
Figure S3: Isoprene experiment (1). APCI-MS measurements of aqueous solutions by direct infusion of liquid solutions, in the negative mode (a) and in the positive mode (b). Mass spectra differences between “dark H$_2$O$_2$” samples and “control” samples show the ions formed during dark oxidation by H$_2$O$_2$ in the aqueous phase.
Figure S4: Isoprene experiment (1). APCI-MS measurements of aqueous solutions by direct infusion of liquid solutions, in the negative mode (a) and in the positive mode (b). Mass spectra differences between “H₂O₂ + hv” samples and “dark H₂O₂” samples show the ions formed during the aqueous phase OH-oxidation of the solution.
Figure S5: Evolution of four identified and quantified reaction products from “control”, “dark $\text{H}_2\text{O}_2$” to “$\text{H}_2\text{O}_2 + \text{hv}$” samples in the mass range 60 – 120 Da (experiment 2). All peak areas were normalized to “control” samples. MB-3-enal = 3-methylbut-3-enal. Quantification was performed using the conditions indicated in Table 1.